INVESTIGATION OF BROMONITROCAMPHANE

BY

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THESIS

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY Paul Meade Ginnings

ENTITLED Investigation of Bromonitrocamphane

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE DEGREE OF Doctor of Philosophy in Chemistry.

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I- INTRODUCTION.

Camphor and its many co-related compounds undergo numerous interesting reactions. Although most of the reactions have been explained satisfactorily, there still remain a few which are somewhat doubtful. Among these is a reaction involving the conversion of camphoroxime into bromonitrocamphane by the action of potassium hypobromite, which was discovered by Forster (2) about twenty years ago. In view of the fact that bromonitrocamphane undergoes so many interesting and unusual reactions, and that its method of synthesis is so unique, it seemed advisable to investigate further the formation of this compound and of others closely related.

II- HISTORICAL.

Forster, after an unsuccessful attempt (1) to prepare alpha-bromo camphoroxime by the direct action of bromine on camphoroxime, tried the behavior of potassium hypobromite on the oxime. He found camphoroxime with this reagent undergoes simultaneous bromination and oxidation to give a compound which he thought at first was a nitroso compound, mainly because of the fact that it gave Liebermann's reaction for nitroso compounds. (2)

In a later paper (3), however, he demonstrated that the compound formed was not a nitroso derivative but a nitro compound, in spite of the fact that it gave Liebermann's reaction for nitroso compounds. The most reasonable structure for this new compound seemed to be

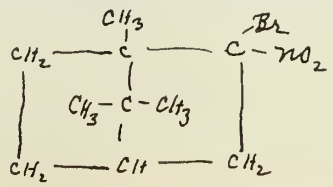

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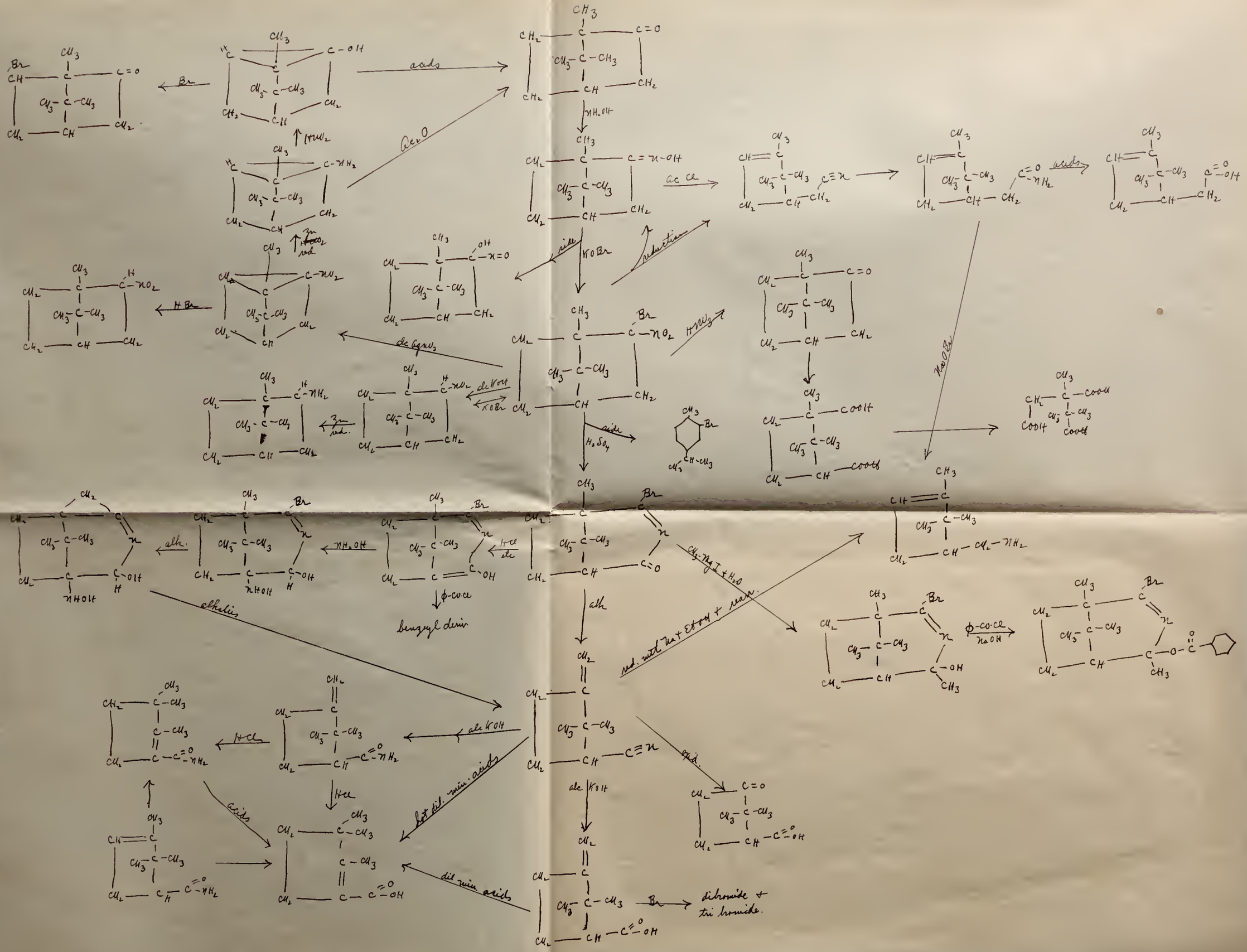
Chart I.


Br
Zn
HCl
acids
Ac₂O
NH₂OH
acetic
NaOBr
reduction
HBr
Br₂
Zn
HCl
dil KOH
HNO₂
H₂SO₄
alk.
NH₂OH
HCl
conc
alkalies
alc KOH
dil min. acids
CH₃-MgI + H₂O
red. with Na + EtOH + warm
ϕ-co-cl
NaOH
benzyl deriv
dibromide +
tri bromide.

which was the structure assigned to it, and it was named 1:1-bromonitrocamphane by Forster.

This compound then became the nucleus of many interesting and unusual reactions. (See chart) On one hand, if it is treated with concentrated sulphuric acid, it loses the elements of water to form a compound which appears to be the anhydride but whose structure has never been satisfactorily solved up to the present time. (4) Under the influence of many mild reagents this anhydride changes readily into an isomer which yields a derivative with benzoyl chloride. Forster proposed several structural formulas for these two isomers but the data he obtained were so conflicting that the question remained open and the structures uncertain. In his latest paper on the structure of these two isomeric anhydrides (4), the structure in greatest favor for the first isomer was that containing a ketone group but all the conventional ketone reagents failed to indicate the presence of a ketone group. Consequently, the question remained unsettled at this point.

A very surprising change takes place when either of the isomeric anhydrides is heated with alkali.(5) The exact mechanism is not known, but eventually an unsaturated nitrile is produced. The structure of this unsaturated nitrile is fairly well established by several facts. On reduction with sodium and ethyl alcohol, alpha-campholeneamine is obtained, the same compound that is produced by treating alpha-campholenic acid amide with sodium hypobromite. This would lead one to suppose that the double bond would be in the ring next to the methyl group but if this is true, it would have the same

structure as alpha-campholytic acid, which compound is already definitely known. Further facts solve the enigma. The unsaturated nitrile, called infra-campholenenitrile by Forster, on alcoholic potassium hydroxide hydrolysis gives an amide entirely different from alpha-campholytic acid amide or beta-campholytic acid amide (iso-lauronolic) but is readily converted into the latter by means of dilute hydrochloric acid, showing that it must be closely realated to both, all three being isomers. The unsaturated acid obtained by careful hydrolysis of the unsaturated nitrile also changes over readily under the influence of acids into beta-campholytic acid. This unsaturated acid, called, "infra-campholenic acid" by Forster, has a free hydrogen alpha to the carboxyl group, indicated by the formation of a tri-bromo acid derivative. All of these facts combined, point to one formula for the unsaturated nitrile. (see chart)

Returning to our nuclear compound, bromonitrocamphane, we find that with alcoholic potassium hydroxide it yields nitro camphane (3) and this on reduction with zinc gives amino-camphane and also beta-bornyl-hydroxylamine. Incidentally this proves the position of the nitrogen atom on the ring. The pseudo form of nitro-camphane with bromine or the normal form with potassium hypobromite, yields the original bromonitrocamphane.

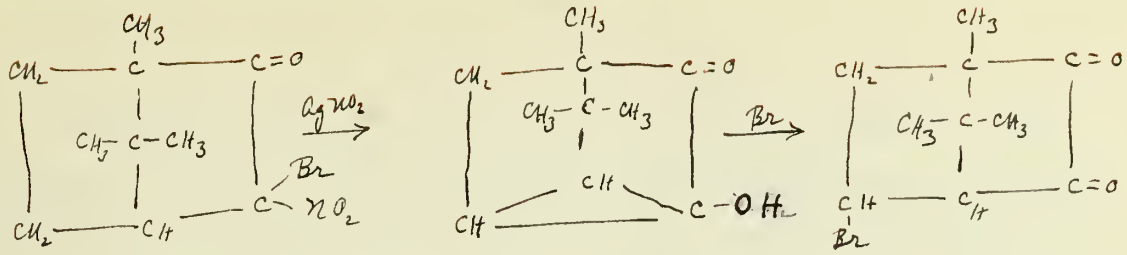
One of the most interesting and unexpected series of reactions takes place when bromonitrocamphane is treated as follows:- If it is allowed to react with alcoholic silver nitrate, it is converted into a compound which Forster first

thought was a camphene derivative. He called it nitro-camphene, (6) although it is really not a camphene derivative, according to the real structure of camphene. The main interest at the time the nitro-camphene was prepared, was that it seemed to open up the road to the preparation of the enolic form of camphor. When the hydrobromic acid is removed from bromonitrocamphane, the ordinary type of unsaturated compound is not produced but a trimethylene ring is formed and this simulates the double bond.(7) The so-called nitro-camphene has many characteristics of an unsaturated compound forming addition compounds with halogens, halogen acids, etc. For instance, addition of hydrobromic acid produces the other bromonitrocamphane which is very similar in some respects to the 1:1-bromonitrocamphane. The nitro-camphene can be reduced with zinc dust and acetic acid to give the corresponding amino-camphene. This with nitrous acid will give the corresponding hydroxy-camphene, and in the first paper of Forster's this compound was thought to be the enolic modification of camphor, although its characteristics were very different from the enolic forms of various di-ketones and ketonic esters. The hydroxy-camphene with dilute mineral acids is changed readily into camphor, but displays no tendency to do so under ordinary conditions, which is rather peculiar. The presence of the trimethylene ring, which simulates the double bond was finally demonstrated by Forster (7) by causing the so-called hydroxy-camphene to react with bromine in glacial acetic acid and sodium acetate. This formed the

compound beta-bromo camphor and showed without a doubt a trimethylene bridge to be present between the two carbon atoms, which would really not be expected to be so far apart according to our valency conceptions of the carbon atom.

The position of the bromine atom in the 1:1-bromonitrocamphane was localized to one of the two top carbon atoms by Forster (8) by his investigation of the decomposition products from the action of concentrated sulphuric acid on bromonitrocamphane to form the anhydride. This was performed by Forster under charring conditions and he isolated as a by-product from this reaction a bromo-cymene, in which the bromine was in the position ortho to the methyl gruup, thus proving the bromine in bromonitrocamphane to be on one of the two top carbons. The tertiary character of the carbon holding the nitro group in the bromonitrocamphane tended to place the bromine on that carbon atom although the proof was not complete at that time. The formation of bromo-cymene here from bromonitrocamphane is very similar to the formation of ordinary cymene from camphor by the action of phosphorus pentoxide.

To generalize on the question of the formation of the trimethylene ring among this type of compounds, Forster (9) tried out a similar set of experiments on bromonitrocamphor. He tried to get the trimethylene ring by removal of hydrobromic acid from bromonitrocamphor, according to more or less of the following order: (on next page)



This would have given theoretically the bromo-camphorquinone ultimately, but when the reaction was tried out, it was found that the bromine and nitro group were broken off to give the unsubstituted camphorquinone. In other words, there was no evidence of the formation of the trimethylene ring as was the case by the removal of hydrobromic acid from the 1:1-bromonitrocamphane.

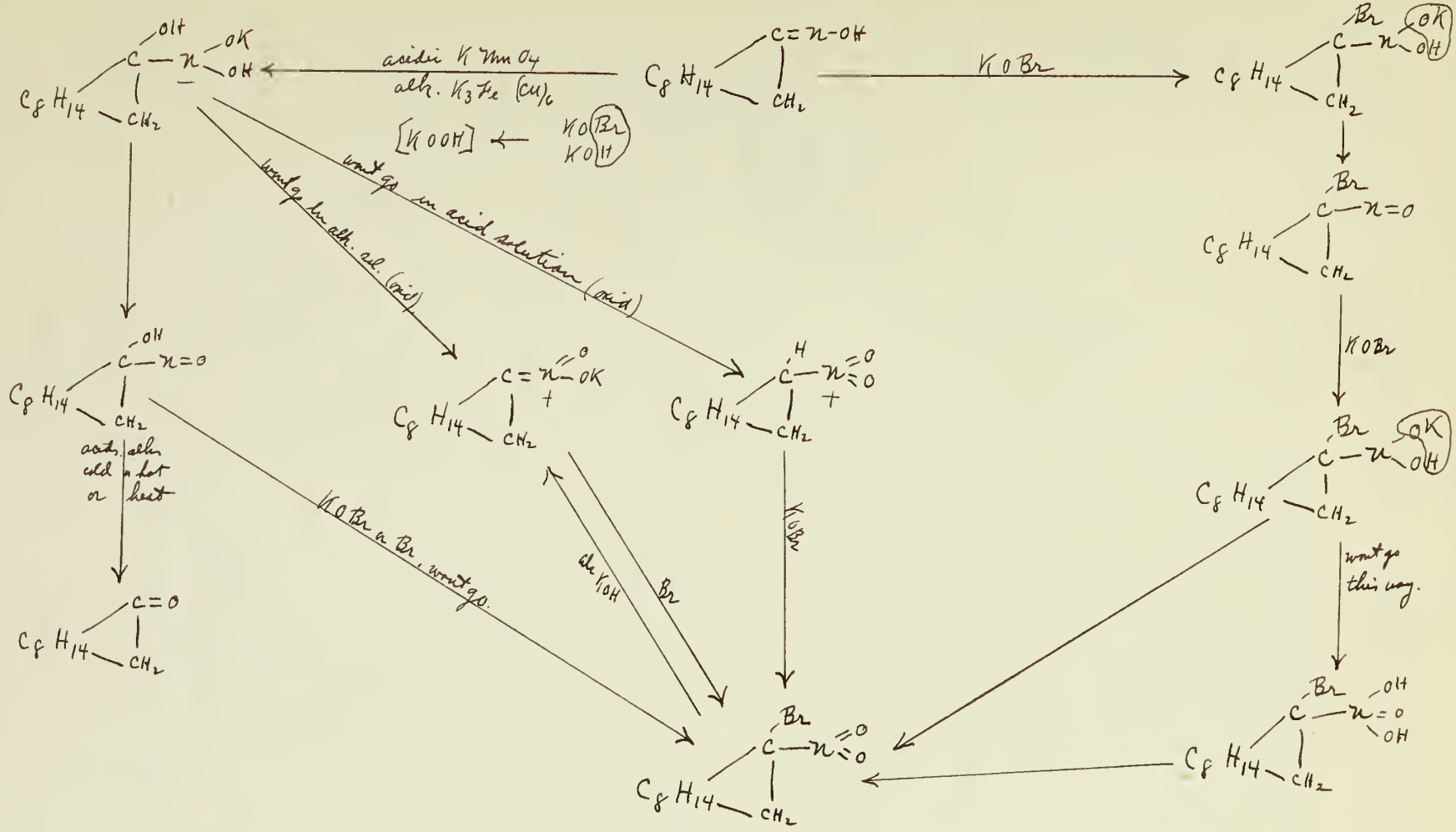
An interesting summary is given by Forster (9) comparing bromonitrocamphane and bromonitrocamphor and their respective reactions.

III- THEORETICAL.

Taking the mass of evidence as a whole, that is, the compounds derived from bromonitrocamphane and the reactions involved to produce them , there seems to be some doubt as to the exact position of the bromine atom in the molecule. The main evidence in support of the fact that the bromine atom is on the same carbon atom as the nitrogen atom, is the fact that bromonitrocamphane behaves like a tertiary nitro compound. Forster in one of his papers on these derivatives (8) isolated a bromine derivative of para-cymene with the bromine atom in the ortho position to the methyl group, thus showing that the bromine atom was on one of the two upper carbons (if bromonitrocamphane is written with the methyl gruup on top). This bromo-cymene derivative was produced as a decomposition product from the action of concentrated sulphuric acid on bromonitrocamphane. Oxidation of the compound bromonitrocamphane should indicate definitely the exact choice of the above two possibilities. This was tried some time ago (10). Although oxidation under many different conditions, with nitric acid and also with a mixture of nitric acid and silver nitrate, was tried, there seemed to be no definite evidence as to the production of either camphoric acid or camphoronic acid. These oxidation experiments have been repeated under still more widely different conditions and more positive results obtained. The main trouble seems to have been that the oxidation was not strenuous enough. Gwinn heated over the steam bath with the

oxidizing agents for varying lengths of time with the result that there was almost always some unchanged bromonitrocamphane remaining in the condenser. This probably contaminated the oxidation products which indicated falsely that a bromo acid was obtained by the oxidation and further indicated that the bromine was in the opposite position in the molecule of bromonitrocamphane. Accordingly, the oxidation has been carried out by the use of dilute nitric acid and constant refluxing for approximately a week or more in time. From the long time oxidation, camphoric acid has been definitely identified and also the barium salt of camphoronic acid separated from the mixture at the end of the oxidation. If the oxidation is carefully controlled under certain conditions, it is possible to isolate considerable quantities of pure camphor as the intermediate stage in the oxidation. All these oxidation products go to substantiate the formula for bromonitrocamphane which has the bromine and nitro groups attached to the same carbon atom. This is to be expected from the synthesis of bromonitrocamphane from camphoroxime by the action of potassium hypobromite.

In the last analysis, the formation of bromonitrocamphane by the action of potassium hypobromite on the corresponding oxime is rather unique. Bromonitro compounds have been made by the action of potassium hypobromite on nitro compounds and bromonitroso compounds by the action of bromine and sodium acetate or pyridine on oximes, but as can be seen, the synthesis involves both bromination and oxidation in order to



Mechanism of the Reaction: 8a. Camphoroxime to Bromonitrocamphane. ZZ

produce both the bromine and nitro groups on the same carbon from the oxime group.

Forster,(3) who first synthesized bromonitrocamphane, suggested that the oxime is changed first to the bromonitrosocamphane and then is oxidized to the bromonitrocamphane. Since a green colored compound is invariably produced on addition of the potassium hypobromite, he suggests this green compound is bromonitrocamphane hydrate which on exposure to air loses water giving the final product, bromonitrocamphane. In view of the fact that this reaction is so unique and it produces a compound which is the nucleus of many other reactions, it seemed desirable to investigate in detail exactly as to the mechanism of its formation.

The first thing observed was that the supposed green bromonitrocamphane hydrate was unaffected by the most vigorous dehydrating reagents. If the impure green mixture produced by the action of potassium hypobromite is taken and treated with concentrated sulphuric acid in the cold and then finally steam distilled, a mixture of camphor and bromonitrocamphane is produced. Simple warming and steam distillation always yield some camphor along with the bromonitrocamphane. Phosphorus pentoxide and phosphorus pentachloride in a boiling solution of the green compound in toluene, benzene, petroleum ether exerted no particular action. All of these facts united probably show no hydrate to be present.

It was next conceived that the green color produced might be due to an intermediate bromonitrosocamphane, as the green

color is characteristic of these nitroso compounds in this series. Accordingly, attempts were made to isolate or prepare by some manner or method the intermediate.

Piloty (11) prepared bromonitrosopropane by the action of bromine on acetoxime in both sodium acetate and also pyridine. So similar experiments were run to prepare the bromonitrosocamphane but there was no action observed.

The next attempt to prepare the hypothetical bromonitrosocompound was by the use of the theoretical amount of potassium hypobromite necessary to brominate but not to oxidize. Although the reaction was carefully controlled, the final result was that approximately one-half of the camphoroxime was changed completely to bromonitrocamphane and the other half remained and was recovered unchanged. This would indicate that the oxidation potential necessary to take the bromonitroso compound to the bromonitro compound was less than that necessary to take the oxime to the bromonitroso compound.

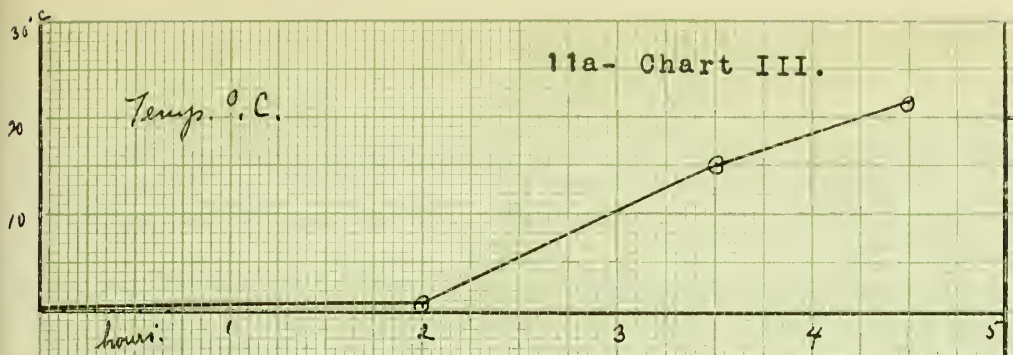
The final evidence which led to the abandonment of this line of endeavor,i.e., the isolation of the intermediate bromonitroso camphane,was that obtained by the quantitative observations on the course of the reaction between potassium hypobromite and camphoroxime. It was hoped that the course of the reaction might be the immediate formation of the bromonitrosocamphane and then the slow oxidation by the remaining potassium hypobromite. Quantitative amounts of the reacting substances were taken and the course of the reaction followed by the removal of aliquot parts of the potassium hypobromite solution, addition to potassium iodide solution, and titration of the

liberated iodine by standard sodium thiosulphate solution. From the data obtained, it is a simple matter to calculate the grams of bromine used up per unit time. In the chart, grams of bromine are plotted against time. The actual curve obtained does not show any break whatsoever at the midway line, thus discouraging any further attempt to isolate directly the intermediate compound in the reaction.

Since it was impossible to prove bromination of the camphoroxime took place first and then oxidation by the potassium-hypobromite, it was deemed advisable to eliminate all of the possibilities except this one. Theoretically, the bromonitro-camphane can be produced by the two main routes from camphor-oxime by the action of potassium hypobromite. One is the route just described above, by the first stage of bromination and subsequent oxidation of the nitroso compound to the nitro compound, and the other is the reversal of the above, which is, oxidation taking place first and bromination last.

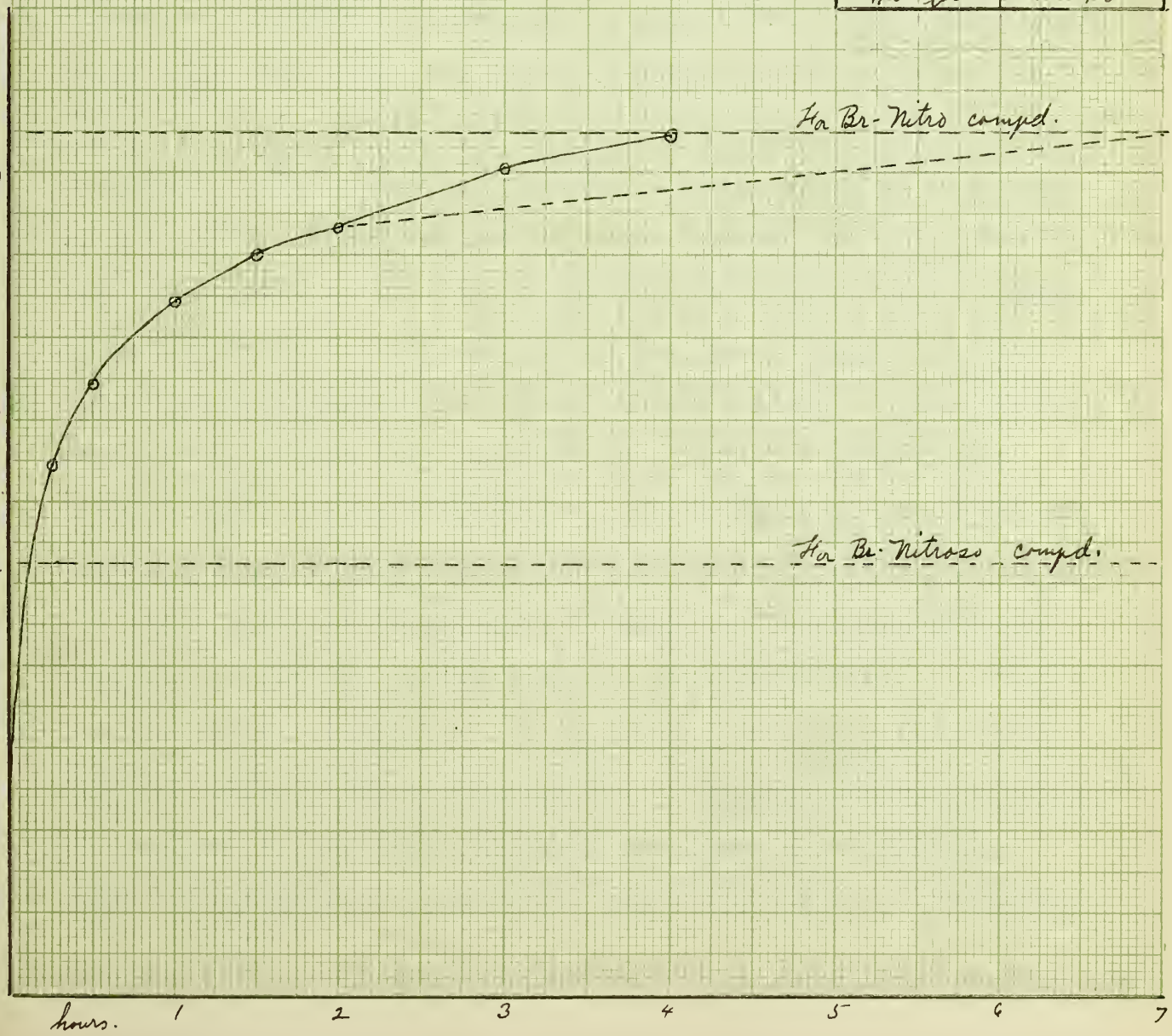
Accordingly, various experiments were run to attempt the synthesis of nitro-camphane from camphoroxime by oxidizing agents. If the nitro-camphane could be produced from camphor-oxime, then it would be a simple matter to obtain the bromo-nitrocamphane by bromination. Theoretically, it is simply a question of which way the intermediate molecule will lose water or potassium hydroxide, to give on the one hand, the hydroxy-nitroso compound and on the other hand the nitro-camphane or its pseudo-nitro form. Examining the situation still further, it is evident that the synthesis by this method would involve the transition from a negative nitrogen atom to a

11a- Chart III.



Time	gms. Br used.
15 min.	6 42
30 min	7 27
1 hr	8 58
1.5 hrs.	9 00
2.0 hr	9 35
3.0 hr	10 05
4.0 hr	10 48

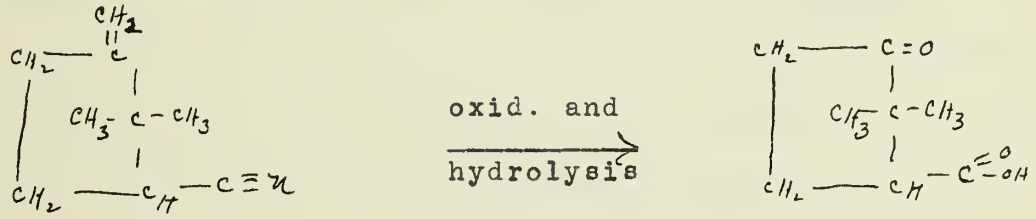
Chart: Action of KOBr on Camphoroxime.



positive nitrogen atom in the nitro-camphane and this would hardly be expected. The actual facts from the experiments bear out this expectation that the change would not take place. Oxidation by dilute acidic potassium permanganate and in another instance by alkaline potassium ferricyanide produced in both cases an hydroxy-nitroso camphane which was first prepared by Forster (12) Furthermore, neither bromine nor potassium hypobromite would transform the hydroxy-nitroso camphane over into the bromonitrocamphane. This eliminates all paths by which the camphoroxime could be oxidized and then brominated to give bromonitrocamphane , leaving the route whereby bromination takes place first and oxidation last. Knowing the above fact , it was possible to so plan the reaction conditions so that the environment would be suitable either for the choice of one route or the other. In no case has it been possible to so control the environment so that the potassium hypobromite acted solely to brominate or to oxidize, but it has been possible to make either one predominate according to one's wishes. By suitable regulation, it has been possible to produce an almost pure white product by the action of potassium hypobromite, with only a slight trace of the blue due to the oxidizing effect. Or, on the other hand, it is possible to make the oxidizing effects predominate and the greater part of the product will be the hydroxy-nitroso camphane. It is evident from the above data, that the supposition of Forster that a bromonitrocamphane hydrate is produced is incorrect and that the green color produced which he observed was not due to the hydrate but to a side re-

action, the simple oxidation of camphoroxime by potassium hypobromite and no bromination of this side product.

In the original work on bromonitrocamphane and its many co-related compounds, Forster prepared a compound which he named infra-campholenic acid and this was made in turn from infra-campholenenitrile. The nitrile can be prepared by the action of concentrated sulphuric acid on bromonitrocamphane to produce an anhydride of unknown structure which with alkali breaks down into the infra-campholenenitrile. Although the structure of this unsaturated nitrile seems certain from the facts as presented by Forster, it seemed desirable to subject this compound to oxidation and examine the products so as to have additional evidence as to its structure. If the structure is correct according to the formula proposed, on oxidation and hydrolysis, it should give:



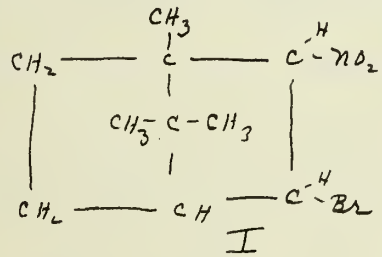
The unsaturated nitrile has been subjected to oxidation by potassium permanganate first in neutral solution to make the di-hydroxy addition product. Acid oxidation can not be used as mineral acids cuase the double bond to shift down into the ring. Accordingly, partial oxidation was effected in the cold by the neutral potassium permanganate. The mixture was acidified and boiled to complete the oxidation and to hydrolyze the nitrile to the acid group. The ketonic acid obtained substantiated the formula originally given to it by Forster.

A study of the preparation of the anhydride was made as the synthesis given originally was rather crude and accompanied by many side reactions. Peculiarly enough, the anhydride can not be produced by the action of phosphorus pentoxide or phosphorus pentachloride in an inert solvent containing the bromonitrocamphane, even after boiling for a long time. The only method seems to be by the action of concentrated sulphuric acid in the cold. Forster ran it under charring conditions with poor results. The reaction has been modified with excellent results by dissolving the bromonitrocamphane in an inert solvent as low boiling petroleum ether and allowing this to flow into a well stirred, cool,mixture of the concentrated sulphuric acid and the inert solvent.

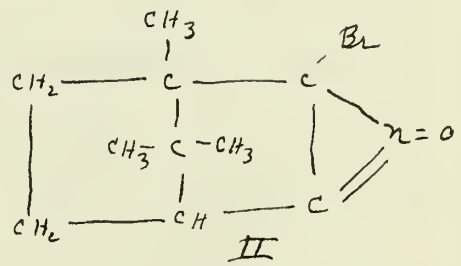
An attempt was made to prepare the Grignard compound with magnesium of both the bromonitrocamphane and also the anhydride, with the ultimate view in mind in the first case to synthesize nitro-camphane by a new method and in the second case to open a path by which better evidence could be obtained as to the structure of the anhydride. But the halogen in both cases was non-reactive in the experiments and the original compound was recovered unchanged. This behavior was rather to be expected from the general rule that the tertiary halogen compounds are not very reactive towards magnesium to form magnesium organohalides.

The question as to the correct structural formula of the anhydride formed by the action of concentrated sulphuric acid on bromonitrocamphane has not been satisfactorily settled. Empirically, the reaction involves simply the removal of the

elements of water to form the anhydride, but, as Forster said, (4) owing to the fact that a nitro group is involved in the dehydration, it is difficult to ascribe a structural formula to the product. From the fact that 2-bromo 1- nitrocamphane as shown below in formula I does not yield an anhydride, it would seem that both of the hydrogens on that carbon atom are involved in the dehydration. But the bromine atom exerts some influence because ordinary nitrocamphane dœs not give an anhydride when treated with concentrated sulphuric acid. On first thought, it would be expected that formula II would represent the correct structure.



I



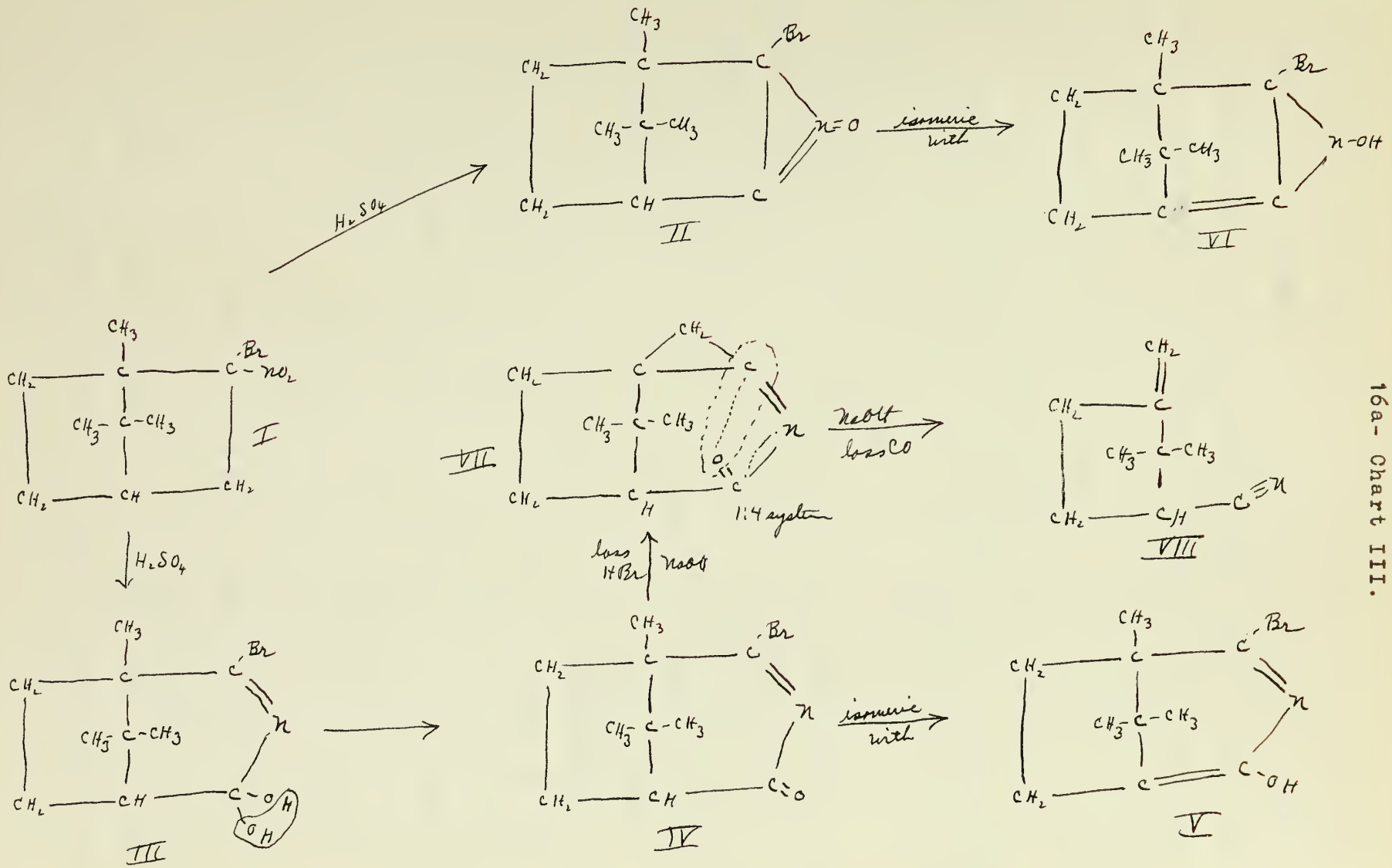
II

It has been found however, that dilute mineral acids and other milder reagents as hydroxylamine, alcoholic ammonia,etc, convert the anhydride to an isomer which gives a benzoyl derivative. Also, this isomer acts as though it was saturated towards bromine and potassium permanganate. These facts with others given later, made it very desirable to investigate further into the correct structure of the two isomeric anhydrides.

Of course formula II is not the only formula that can be ascribed to the first anhydride. Very pertinent to this question is the work of Wallach (13,14) on the action of sulphuric acid on various oximes. He has shown that in many cases the first step in the reaction is the rearrangement of the oxime

to the lactam compound which might be represented as follows:

In other words, what happens is that the oxygen supply from the nitrogen atom rearranges on to the carbon adjacent to the nitrogen atom and the hydrogen remains on the nitrogen, the lactam being ultimately formed with one more member in the total number of atoms in the ring. It is of course not impossible that a slightly similar action may have taken place in the course of the action of sulphuric acid on bromonitrocamphane. (see next page for formulas) The first step according to this mechanism would be the rearrangement of the nitrogen atom into the ring and the oxygen atoms from the nitro group onto the adjacent carbon. One carbon is blocked by the bromine atom and the other carbon has two hydrogens so we should expect the two oxygen atoms would form two hydroxy groups. (formula III) Then , of course, the elements of water would be lost, leaving us a ketone group for that section of the molecule. This is the mechanism shown graphically in the formulas, III and IV. Formula IV explains more reactions of the anhydride than does II. For instance, when the anhydride is treated with alkali, the unsaturated nitrile, VIII is produced. Probably the intermediate is the immediate loss of hydrobromic acid to form the temporary trimethylene ring compound and then this loses carbon monoxide to give the unsaturated nitrile. It is possible that Thiele's 1:4 partial valences may have something to do with the loss of carbon mon-



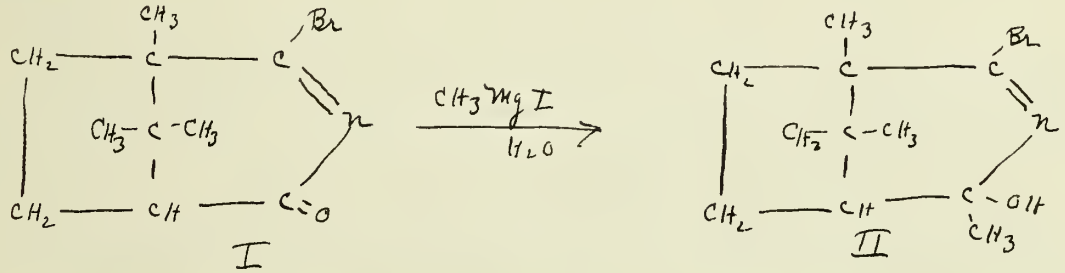
16a- Chart III.

oxide is rather remarkable and yet in another way, it is not so surprising. Consider the formula IV. It might be said to be a ring compound of a substituted inner amide. This same grouping is present in a strained condition in the intermediate, formula VII. It is a common fact that amides in general lose water to form nitriles. Perhaps it is then not too far fetched to say that a slightly similar reaction takes place in this case, the carbon on the nitrogen joins with the oxygen on the other carbon, formula VII, and carbon monoxide is liberated to give the unsaturated nitrile.

Forster proposed the formula IV for the anhydride but was unable to prove that it was actually the correct formula. If the ketone group alone is considered, it should give the regular ketone reactions with such reagents as hydroxylamine, phenyl-hydrazine etc, but Forster obtained a hydroxylamino compound by treatment of the anhydride with hydroxylamine. If the ketone were present, it had evidently rearranged to the enol form and reacted as such. He was unable to prove that the ketone grouping actually existed, although that seemed the logical formula with which to represent the anhydride. The main trouble lies in the ease with which the first anhydride rearranges with comparatively weak reagents into its isomer, supposedly the enol form as it gives a benzoyl derivative.

It seemed that the action of the Grignard reagent on the first anhydride isomer (formula IV probably) might shed some light on the structure of the two isomeric anhydrides. Accordingly, the anhydride was treated with the Grignard reagent,

in this case, methyl magnesium iodide, and the compound formed decomposed with water giving a new compound or derivative of the anhydride. It is easily purified in beautiful crystals and analysis indicates that the molecule has gained the equivalent of one CH_4 molecular weight, which is to be expected if the ketone group is present. From this and other data given later, combined with the fact that this compound yields acyl derivatives with acylating agents, such as acetic anhydride, benzoyl chloride, the structural changes should be represented as follows:

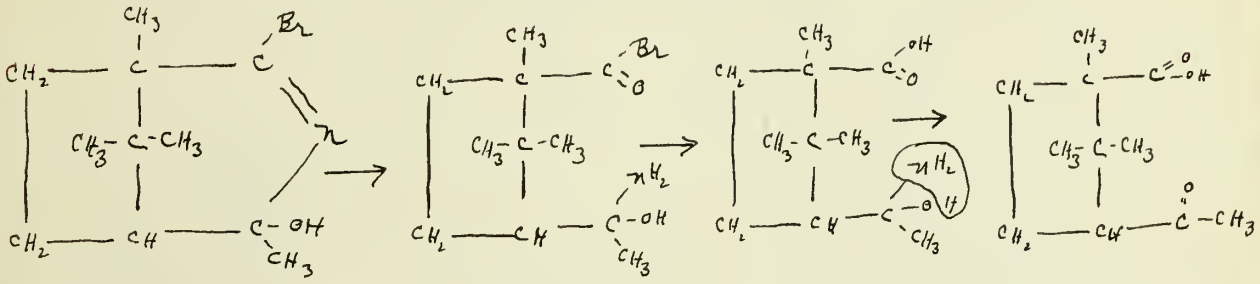


I II

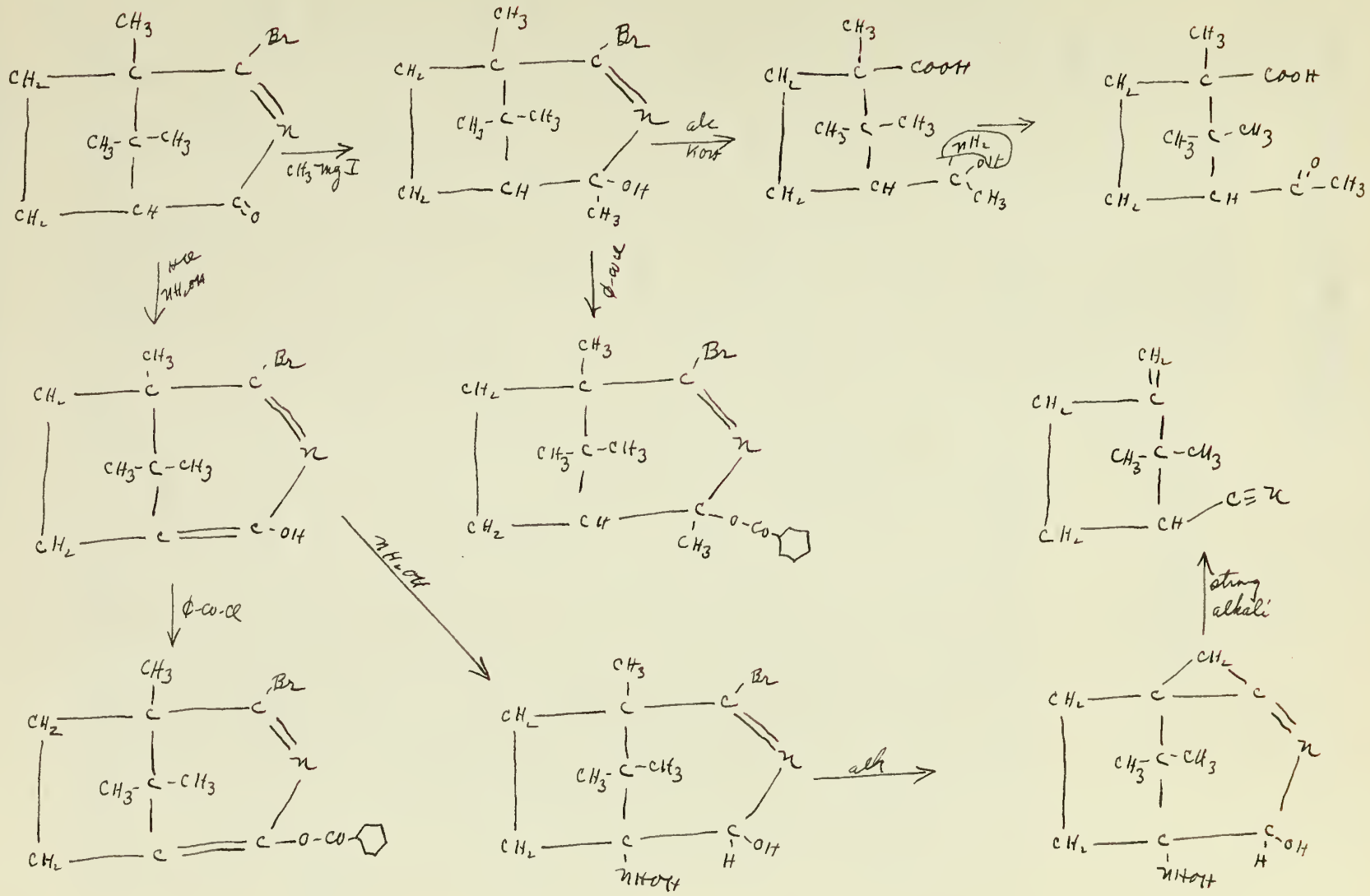
So the correct formula for the first anhydride should be that as shown above and the isomeride probably as the enol form of the ketone.

After having prepared the derivative by means of the action of methyl magnesium iodide on the first form of the bromo-nitrocamphane anhydride, it was conceived that it might be interesting to know the result of the action of alcoholic sodium hydroxide on this compound. (formula II) Accordingly, it was treated with alcoholic sodium hydroxide and the following changes took place:- bromine was lost from the compound, probably forming sodium bromide, the nitrogen atom was lost in the form of ammonia, which was detectable by litmus paper in the alcoholic vapors, by the formation of ammonium chloride, and by the use of Nessler's reagent. The product was an acid

which gave the iodoform test for the grouping $-CO-CH_3$ and melted from 67-70 degrees C. The logical compound that would be formed which has a place here is the following methyl ketonic acid which has a melting point of 68-9 degrees C. The structural changes involved could be represented as follows:



This furnishes even more confirmatory data for the inner substituted amide formula for first form of bromonitrocamphane anhydride. In other words, it completes the proof for this structural formula for the first form of the bromonitrocamphane anhydride and supplements Forster's data for the isomeric compound, the enol form for this same anhydride,


CH3-mg I
alc KOH
NH2OH
ϕ-co-cl
NH2OH
alk
strong alkali

IV- EXPERIMENTAL.

1- Preparation of Camphoroxime.

Materials:

150 grams of camphor.

70 grams of hydroxylamine hydrochloride.

200 grams of sodium acetate.

2500 cc. of 95 % alcohol.

150 grams of pure camphor are dissolved in about 2500 cc of 95 % alcohol and heated to boiling on the steam bath. 200 grams of sodium acetate are added to this hot solution and just enough water that the whole forms a homogenious solution. Then 70 grams of hydroxylamine hydrochloride are dissolved in the least amount of water possible and added to the alcoholic solution in portions and the whole solution refluxed for about two or three days to complete the reaction. At the end of this time, the alcohol is distilled off on the steam bath and the residue diluted with cold water to about 5 liters volume which precipitates out the solid camphoroxime which can be easily filtered off with suction and dried. If the pure oxime is wanter, it can be crystallized out of ligroin, m.p. 118 degrees C. Yield is practically quantitative, if the pure hydroxylamine is used.

Remarks: Pure hydroxylamine hydrochloride should be used as any impurity decreases the yield of the oxime considerably. Also, the alcoholic solution during the reaction should contain the least amount of water possible to form a homogeneous solution.

2- Preparation of bromonitrocamphane.

(The method used, with slight variations, is almost identical with that used originally by Forster (2) to prepare the above compound)

Materials:

600 grams of potassium hydroxide or 500 of sodium hydroxide.

800 grams of bromine.

100 grams of camphoroxime.

Procedure:

600 grams of potassium hydroxide are dissolved in about one liter of water in a 5 liter r.b. flask fitten up with a rapid mechanical stirrer and cooled to below 0 degrees C. Crushed ice is added to the potassium hydroxide solution and a thin stream of liquid bromine is allowed to run in from a separatory funnel, care being taken that no local heating takes place and that there is always some excess ice in the solution in the flask to insure it remaining at or below 0 degrees C. As soon as the 800 grams of bromine have been converted to the potassium hypobromite solution, 100 grams of camphoroxime in a finely powdered state are added in small portions to the well stirred liquid containing suspended ice. The mixture is allowed to react under the influence of vigorous stirring for several hours and at the end of this time sufficient water is added to bring the water up to 5 liters and the bromonitrocamphane is filtered off with suction and dried. When dissolved in hot concentrated alcohol and cooled, the bromonitrocamphane crystallizes out in white fern like crystals, m.p. 220 degrees C. The yield is practically quantitative.

Remarks:

It is very desirable that the solutions should be kept at at least 0 degrees C. to obtain a quantitative yield. It will be noticedthat 800 grams of bromine were used instead of 400 grams as directed originally by Forster in his paper. It has been found that use of the smaller amount shows a tendency to the formation of the green compound, the hydroxy-nitroso derivative produced by the oxidizing action of the potassium hypobromite on the camphoroxime. If the larger quantity is used, practically none of the green nitroso compound is formed and the product is pure white, differing from the green compound obtained by Forster. As has been shown elsewhere in this paper, the green compound is not the hydrate of bromonitrocamphane nor the intermediate bromonitrosocamphane but is the compound formed as a side reaction by the oxidizing action of the potassium hypobromite on the camphoroxime. The same compound can be prepared by the action of acidic potassium permanganate on camphoroxime, and this by further action by potassium hypobromite does not yield bromonitrocamphane, which would be expected if the green nitroso camphane were an intermediate of the regular complete reaction. Sodium hypobromite can also be used with success, the same molar quantities of sodium hydroxide being used but of course different actual weight in grams.

3- Oxidation of bromonitrocamphane with dilute nitric acid.

Materials:

25 grams of bromonitrocamphane.

200 cc of water.

300 cc concentrated nitric acid.

Procedure:

The above mixture was refluxed in a ground glass connected, water cooled reflux apparatus for seven days and nights. At the beginning of the oxidation, much of the bromonitrocamphane condensed in the cool condenser tube and at different intervals this was washed down carefully with small amounts of ether. After the oxidation had proceeded for a few hours, it was not necessary to wash the tube with ether as the material has assumed an oily consistency which washed back with the nitric acid. At the end of the oxidation, the solution was cooled and extracted several times with ether. The nitric acid layer was evaporated down on the steam bath until an oily semi-solid mass remained which was then dissolved in ammonium hydroxide, excess ammonia boiled off and barium chloride added to the hot solution, a white precipitate,about four grams, being obtained immediately and more forming on further heating. This was presumably the barium salt of camphoronic acid as the original semi-solid mass was fairly insoluble in ether. Identification was not necessary as both camphoric acid and camphor were both isolated later as decomposition products.

The original ether extract was treated with sodium hydroxide to take out the acids, the acids being liberated by hydrochloric acid, addextracted with a new portion of ether. This was evaporated almost to dryness on steam bath, treated with acetic anhydride and a drop or so of acetyl chloride to convert the camphoric acid present to the anhydride. After heating this

for a short time, it was cooled, diluted with water, extracted with a large volume of ether to take out the free organic acids and anhydrides, washed thoroughly with cold sodium carbonate solution to remove the free acids leaving the anhydride in the ether layer. The sodium carbonate was washed out of the ether by water, the ether solution dried, and this upon evaporation almost to dryness with as little heat as possible to prevent any hydrolysis back to the free acid, and the residue dissolved in hot concentrated alcohol gave one gram of fine needles, m.p. 220 degrees C. on cooling the alcoholic solution. Mixed m.p., no lowering. Hydrolysis of the camphoric anhydride obtained, changed it to the free acid gave crystals melting slightly lower that 178 degrees C. probably due to the ease with which the free acid changes over into the camphoric anhydride during the m.p. determination.

4- Oxidation of bromonitrocamphane to camphor.

Materials:

50 grams of bromonitrocamphane.

200 cc. of water.

300 cc of concentrated nitric acid.

Procedure:

In this experiment, the same procedure was followed as the one where the camphoric acid or rather the anhydride was isolated. As usual, at first, the bromonitrocamphane condensed in the cool water jacketed condenser tube, which was washed down with ether. After a time, the bromonitrocamphane

ceased to condense and an oil seemed to return to the flask instead. Then in its turn, a white solid collected so much in the condenser that it became clogged. It was suspected that it might be different from the original compound which prompted the disconnection of the condenser tube proper and the washing out of the solid with ether. When this white solid was crystallized out of alcohol, it gave crystals melting at 176 degrees C. the same as that of camphor. About 7 grams of camphor were obtained at this step in the oxidation.

5- Investigation of the so-called "hydrate" compound.

This green compound, produced during the action of potassium hypobromite on camphoroxime was supposed by Forster (3) to be the hydrate of bromonitrocamphane. If so, and if water is lost by drying in air, then the ordinary dehyrating agents should dehydrate the hydrate giving the plain bromonitrocamphane.

The action of cold concentrated sulphuric acid was tried (by the same procedure as given under the preparation of the bromonitrocamphane anhydride) on the green compound and both the anhydride of the plain bromonitrocamphane and camphor were obtained This is no duubt due to the fact that part of the green mixture was present as the real bromonitrocamphane and part as the nitroso compound as proven later on in this paper.

An ordinary solution of the green mixture produced by the action of potassium hypobromite gives both the bromonitrocamphane andcamphor on steam distillation.

Warming of a solution of the green compound causes the color to turn yellow and then this by distillation with steam

yields camphor. Bromonitrocamphane is always present when the green compound is produced by the action of potassium hypobromite on the camphoroxime.

The green mixture obtained by the action of potassium hypobromite was also exposed to the action of phosphorus pentoxide and phosphorus pentachloride in the cold in inert solvent of petroleum ether, toluene, benzene etc, both in hot and cold solution. No action was observed in the cold and the action on heating was only that which is also noticeable when the pure solution in the inert solvent is also heated up. If the green compound was an ordinary hydrate, it should have formed the bromonitrocamphane very easily by these dehydrating agents.

6- Attempt to prepare the bromo-nitroso camphane by the action of bromine on the camphoroxime in glacial acetic acid and sodium acetate.

This attempt was more or less the same as the experiment or attempt of Forster to prepare alpha-bromocamphoroxime by the action of bromine in acetic acid. Sodium acetate was used in this experiment to take care of the possible halogen acid liberated but no action was observed.

3.35 grams of camphoroxime were dissolved in glacial acetic acid (50 cc.) and about 10 grams of sodium acetate added and 30 grams of bromine run in slowlyto the well stirred solution. But no action took place and the camphoroxime was recovered unchanged.

7- Attempt to synthesize bromonitrosocamphane by the action of bromine on camphoroxime in pyridine solution.

This attempt was modeled after the procedure used to synthesize the aliphatic bromonitroso compounds. (11) 6.68 grams of camphoroxime were dissolved in about 20 cc. of pyridine in a one liter flask with mechanical stirrer, cooled to a low temperature below zero degrees, and about 7 grams of bromine added slowly by means of a dropping funnel. The first action was the addition of the bromine to form the deep bichromate red color of the pyridine addition compound but this on slight warming decomposed to give the pyridine and bromine again. But the mixture was without action on the camphoroxime. The reaction mixture should be characterized by the deep green or blue color of the nitroso compound which is such a valuable test for the ketones etc in the aliphatic series. The tendency for the bromine to add on to the double bond between the carbon and the nitrogen is very small nor will it add with glacial acetic acid and sodium acetate as shown elsewhere and also by Forster originally.

8- Attempt to prepare the bromonitrosocamphane.

Materials:

33.5 grams of camphoroxime.

16 grams of bromine.

40 grams of potassium hydroxide and also 10 grams.

Procedure:

10 grams of potassium hydroxide were dissolved in 200 cc

of water in a one liter flask, r.b. and about 500 cc of ether containing 33.5 grams of camphoroxime were added on top of the potassium hydroxide solution. The flask was fitted up with a stirrer and the mixture was cooled to about -10 degrees C. Meanwhile a potassium hypobromite solution was prepared by adding 16 gramsof bromine to 40 grams of potassium hydroxide solution contained in 150 cc of aqueous solution. This was cooled to the same low temperature. The the potassium hypobromite was added slowly to the mixture in the flask with crushed ice to insure cooling.

The ether layer was finally separated at the end of the reaction and steam passed through an aqueous solution. Received 27.5 grams of the bromonitrocamphane by distillation, or 56 % theoretical for the complete formation of bromonitrocamphane if plenty of potassium hypobromite were used. Then about 10 grams of the camphoroxime were recovered from the residue and presumably the rest was lost through the alkaline solution of also thruugh the formation of the green compound which has been proven elsewhere to be the hydroxy-nitroso camphane. From this experiment, it would seem that if there was an intermediate bromonitroso camphane molecule formed, that is is immediately oxidized by the action of more potassium hypobromite to the bromonitrocamphane instead of more of the bromonitrosocamphane being formed by the potassium hypobromite.

The quantitative observations in the next experiment show fairly conclusively that this is the case.

9- Quantitative observations on the course of the action of potassium hypobromite on camphoroxime.

Working on the theory that possibly there might be an intermediate bromonitroso compound formed and that accordingly there might be a definite variation or break in the curve of the utilization of the potassium hypobromite, the following set of experiments were run to determine whether any sharp variation took place in theeaction of the potassium hypobromite.

It might possibly be that an immediate addition of one mole of potassium hypobromite takes place and then a slow oxidation of the bromonitroso compound to the bromonitrocamphane by the action of another mole of potassium hypobromite.

Accordingly, exactly 6.70 grams of pure camphoroxime were taken in ether solution, and put in with a rapid mechanical stirrer with 10.50 grams of bromine in 200 cc of potassium hydroxide, the temperature meanwhile being kept as close to zero degrees as possible. After 15 minutes had elapsed, a sample of 2 cc of the potassium hypobromite solution was removed by means of a graduated pipette, diluted, 10 cc of potassium iodide solution (100 grams per liter) added, and then 10 cc of dilute hydrochloric acid to liberatethe hypoiodous acid. This in turn acted on the potassium iodide, liberating iodine and it was titrated with standard sodium thiosulphate solution, using starch as an indicator, to the end point. By removing suitable aliquot parts at various time intervals and titrating the oxidizing power of the potassium hypobromite remaining in the aqueous solution, the grams of unutilized bromine remaining

could be calculated. Then this can be easily interpreted so that ultimately the grams of bromine used per unit time can be plotted against time. The curve was plotted (see under theoretical) but there was no sharp break in the curve. At the end of two hours and one-half, the curve was assuming an almost parallel course with the axis so the temperature was raised and so the reaction went to completion. Interpreting the curve, the oxidation potential required to oxidize bromonitrosocamphane to bromonitrocamphane is less than the oxidation potential for the oxidation of camphoroxime to bromonitrosocamphane. Therefore as soon as any bromonitrosocamphane is formed, it is immediately oxidized to the nitro compound before another mole of camphoroxime is changed to the bromonitroso compound. These quantitative results thus discouraged effectively any further attempts to isolate the intermediate bromonitrosocamphane.

10- Preparation of the hydroxy-nitrosocamphane by the action of acidic potassium permanganate on camphoroxime.

This reaction was first run by Forster (12) and the procedure used here was essentially the same.

An attempt was made to see if the green nitroso compound produced by the acidic oxidation of camphoroxime by potassium permanganate could be converted into bromonitrocamphane by the action of potassium hypobromite, but it was found that camphor was regenerated.

Bromine in acetic acid and sodium acetate exerted no effect on the hydroxy-nitrosocamphane.

From the above data, it appears that the green compound is neither the hydrated nitro compound nor the intermediate bromonitroso compound but purely a side reaction from the main route.

11- Action of potassium ferricyanide on camphoroxime in alkaline solution.

3:35 grams of camphoroxime were dissolved in about 50 cc of concentrated potassium hydroxide, cooled to about 0 degrees, and an aqueous solution of potassium ferricyanide (13.2 grams) added drop by drop by means of a dropping funnel. Almost immediately, a white flocculent precipitate began to form which turned to a bluish green color The reaction was allowed to proceed for about one-half an hour when it was diluted to one liter with distilled water and the bluish green compound filtered off by suction. Dried on a filter plate, it gives the same unstable hydroxy-nitroso compound in almost quantitative yields as prepared originally by Forster by the acidic oxidation with potassium permanganate. However, this is a much better method for the preparation than by the oxidation with acidic permanganate.

12- Control of reaction with potassium hypobromite to produce the hydroxy-nitrosocamphane as the main product.

The conditions of the reaction of the potassium hypobromite on the camphoroxime can be so varied so as to give pure bromonitrocamphane or to give primarily the hydroxy-nitrosocamphane.

For the preparation of the pure bromonitrocamphane with practically none of the hydroxy-nitrosocamphane, an excess of bromine and addition of the dry powdered camphoroxime is essential as described in detail elsewhere in this paper.

For the production mainly of the hydroxy-nitrosocamphane, by the use of potassium hypobromite, take the following procedure:- Take 3.35 grams of camphoroxime in about 300 cc of ether over 200 cc of aqueous solution containing 40 grams of potassium hydroxide and added the bromine slowly to this well cooled solution. The ether solution immediately begins to take on the emerald green color characteristic of the hydroxy-nitrosocamphane. Some of the bromonitrocamphane is of course produced, but this modification above has a tendency to cause the oxidation effect of the potassium hypobromite to predominate and assert itself immediately on the camphoroxime.

13- Oxidation of infra-campholenenitrile by the action of potassium permanganate.

About 20 grams of the infracampholenenitrile were taken and placed in a one liter flask equipped with a mechanical stirrer with about 600 cc. of water and 500 cc. of a 3 % solution of potassium permanganate run in slowly. The flask was kept cool for the first part of the reaction in order to cause the production as far as possible of the di-hydroxy compound of the nitrile. Acid oxidation at this point can not be used as strong mineral acids cause the rearrangement of the double bond down to the corresponding alpha-campholytic nitrile.

Consequently, alkaline oxidation was used to obtain the di- hydroxy compound and then the solution was made acid and oxidized further by the vigorous acid oxidation for several hours. The excess of the oxidizing agent, mainly the manganese dioxide, was decomposed by the addition of sodium sulfite and the cold solution extracted several times with ether, the ether layer then being put in flask with condenser and hydrolyzed with strong alkali for several days to hydrolyze the nitrile to the acid. At the end of this time, the reaction mixture was acidified with acid, extracted several times with ether, the ether extract treated with alkali to take out the acids formed, including the ketonic acid wished, the non-acid portion being removed by the ether from the alkali. Then the acids were liberated from the ether by acid, extracted several times from the cold aqueous solution (as the ketonic acid is somewhat soluble in water) with ether, the ether evaporated almost to dryness and a small amount of water added which was then heated to boiling On allowing the aqueous solution to cool slowly over night, there crystallized out a very small amount of long needle like crystals on the side of the test tube. These were transferred to a melting point tube and they began to melt or soften at 107 degrees, finishing melting at 110 degrees C. (Melting point of the ketonic acid is 109-11 degrees C) The slight lowering is probably due to a slight impurity in the crystals.

14- Preparation of bromonitrocamphane anhydride.

Materials:

1 liter of concentrated sulphuric acid.

400 cc. of petroleum ether, b.p. 25-40 degrees best.

100 grams of bromonitrocamphane.

Procedure:

One liter of concentrated sulphuric acid was put in a 3 liter r.b. pyrex flask which was connected up to a mechanical stirrer. This was surrounded with an ice and salt mixture and about 100 cc. of the petroleum ether added to the sulphuric acid. While the sulphuric acid mixture was cooling down to -10 degs. C., 100 grams of pure bromonitrocamphane were dissolved in about 300 cc of petroleum ether (same as above). This was placed in a separatory funnel and allowed to drop slowly into the cool mixture of the sulphuric acid and petroleum ether. The sulphuric acid turned slightly yellow, then from orange to deep red but did not turn brown or black, as observed by Forster in his similar method. Nor were any decomposition products observed when this method was run carefully. After a short time, usually about one-half hour, the stirrer was removed, and the petroleum ether rises to the top in a layer. This contains some of the bromonitrocamphane anhydride but most of the anhydride is in the sulphuric acid layer. The two layers should be separated here at this point, and the sulphuric acid poured with stirring onto finely crushed ice which precipitates a flocculent white solid. This is either filtered off after dilution with water, or it can be dissolved and extracted out with ether. It is the washed with sodium carbonate solution to remove the last

traces of the acid, washed again with water, and the ether removed by evaporation on the steam bath. The residue can then be crystallized from concentrated hot alcohol to give an almost quantitative (70- 100 % yields) of the bromonitrocamphane anhydride.

Remarks:

Forster in his paper used almost the same method except that he added his bromonitrocamphane compound directly to the concentrated sulphuric acid with the result that he caused considerable local heating with charring and under these charring conditions, a lot of undesirable by-products were formed. By the use of the above method that I have described, the dehydrating action is toned down, so to speak, so that the heat produced can be controlled and the decomposition products are eliminated entirely and the product obtained is almost pure white without recrystallization. When the petrol ether solution of the bromonitrocamphane is added to the mixture of the sulphuric acid and pure petrol ether, it seems that the bromonitrocamphane is almost immediately taken over into the sulphuric acid and dehydrated at once. Considerable heat is produced by the action of the sulphuric acid on the bromonitrocamphane but this is compensated for by the ice and salt bath aided by very vigorous stirring so that the temperature never rises above -5 degs C. Any greater rise of temperature during the addition of the petroleum ether solution of the bromonitrocamphane decreases the yield of the anhydride.

The main point about this modification of Forster's method is that it enables the operator to keep the reaction well in

hand and prevents local heating effects and subsequent decomposition.

15- Attempt to prepare the organo-magnesium compounds of the bromonitrocamphane and also the bromonitrocamphane anhydride.

The attempt to prepare the magnesium halide compound of bromonitrocamphane was mainly in hopes that it would furnish a better method for the preparation of nitrocamphane. The regular procedure for the preparation of Grignard reagent was used, suspension of magnesium in ether with the halide compound and addition of some iodine as a catalyst for the reaction. But the bromonitrocamphane would not react under any of the conditions tried even under long refluxing and also after the addition of a small amount of methyl iodide. The original compound was recovered unchanged The non-reactivity of the halogen was more or less to be expected since it is a tertiary halogen and the tertiary halogen compounds in general react with difficulty with magnesium.

The same regular procedure was tried with the first form of the bromonitrocamphane anhydride and the same results were obtained, the halogen being also non-reactive in this compound. The idea here was to furnish some means by which the true structure of the anhydride compound could be more clearly elucidated.

16- Action of the Grignard reagent on the bromonitrocamphane anhydride. Methyl magnesium iodide being used.

Materials:

10 grams of bromonitrocamphane anhydride.

20 grams of methyl iodide.

5 grams of magnesium turnings.

250 cc of dry ether.

Procedure:

5 grams of magnesium turnings are immersed under 200 cc of dry ether in a one liter flask connected to a reflux condenser with air tight connections. A small amount of iodine is added as a catalyst to the flask and 20 grams of methyl iodide added in portions so that the vigorous reation is well under control until all is added. The solution is refluxed until all action has ceased and when there is only a very small amount of magnesium left in the bottom of the flask. Then 10 grams of the bromonitrocamphane anhydride are dissolved in about 50 cc. of dry ether and added in small portions through the top of the condenser and this mixture refluxed for several hours when the flask is disconnected, and small amounts of water added cautiously to decompose the Grignard compound. Then after the main reaction has ceased, some dilute sulphuric acid is added. The whole is stirred well, at least for several minutes and the ether separated off by means of a separatory funnel, washed with water, sodium carbonate, again with water several times, dried over calcium chloride and evaporated down almost to dryness over the steam bath. At this point, if the liquid residue is allowed to cool slowly so that the last portion of the ether evaporates off spontaneously, the derivative crystallizes out in large lustrous transparent places,m.p.117-8 degs.C.

It is insoluble in acids, and alkalies, soluble in ether and alcohol but insoluble in water. It isconverted readily into the corresponding acyl derivatives. Analysis of the oompound formed by the action of methyl magnesium iodide on bromonitro-camphane anhydride:

.1705 gms. gave .1230 gms. AgBr or .0524 gms bromine.

Found for the % Br 30.73 %

Theory, $C_{11}H18ONBr$ 30.75 %

By treating the above compound with benzoyl chloride and sodium hydroxide according to the Schotten-Baumann reaction, a benzoyl derivative is obtained fine crystals out of the hot dilute alcohol. m.p. 113-4 degs C. It will also crystallize from ether in star shaped needle colonies. Analysis of this benzoyl derivative of the first compound gave:

.2141 gms gave .1094 gms AgBr or 21.75 % Bromine.

Theory for the compound $C_{18}H_{22}O_2NBr$ is 21.90 % Bromine.

17- Action of alcoholic sodium hydroxide on the compound produced by the Grignard reaction (see16).

To observe the action of alcoholic sodium hydroxide on the compound produced by the action of methyl magnesium iodide on bromonitrocamphane anhydride, about 5 grams of this deriv-ative were dissolved in about 25 cc. of ethyl alcohol and 10 cc. of concentrated sodium hydroxide added and the mixture or solution boiled for a few minutes. A strip of red litmus wetted and suspended in the vapors issuing from the flask was turned red, while clouds of ammonium chloride were produced when an hydrochloric acid bottle was brought in proximity, and

the vapors turned a portion of Nessler's solution a deep carmine red, all showing the loss of ammonia. The alcohol is boiled off, the residue taken up in ether and water together, acidified with acid, extracted with ether, the acids extracted from the ether with sodium hydroxide and the acids again liberated from the alkali by acid and removed to the ether layer. This was evaporated spontaneously the rest of the way, whereby slight yellowish crusts separated out, which are soluble in alkali,but insoluble in water. A sample of these crusts when tested according to the iodoform reaction gave a heavy precipitate of iodoform. Melting point gave 67-70 degrees C. The wide range of the temperature was probably due to slight impurities as the quantity was too small to purify as much as desired. The compound gave negative qualitative tests for halogen and nitrogen, It was undoubtedly the methyl ketonic acid that would be expected if the structures of the preceding compounds were as supposed.

V-SUMMARY.

1- Bromonitrocamphane on oxidation with nitric acid breaks down successively into camphor, camphoric acid, and camphoronic acid.

2- The course of the action of potassium hypobromite on camphoroxime has been found to be bromination of camphoroxime and then oxidation to the bromonitrocamphane. No bromonitrocamphane hydrate is formed as was supposed by Forster.

3- Potassium hypobromite may also act as an oxidizing agent on camphoroxime to produce hydroxy-nitroso-camphane.

4- Strenuous permanganate oxidation of infra-campholenenitrile and hydrolysis ultimately yields the corresponding ketonic acid.

5- Bromonitrocamphane anhydride has been prepared by an improved method and the structure of the anhydride elucidated by its behavior with the Grignard reagent, methyl magnesium iodide. Since the structure of the anhydride is now an established fact, a logical explanation is provided for the unexpected transition from bromonitrocamphane to infra-campholenenitrile.

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VII- VITA.

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Publications:- "Syntheses of Chromanes and Coumaranes" Journal of the American Chem. Soc. Vol. 42, 157, (1920) by R. E. Rindfusz, P. M. Ginnings, V. L. Harnack.

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